<Division of Environmental Chemistry> Solution and Interface Chemistry

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- Solution and Interface Chemistry -

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Visitors

Prof BEN-NAIM, Arieh	The Hebrew University of Jerusalem, Israel, 9 - 10 March 2004
Prof BOPP, Philippe A.	Universite Bordeaux I, France, 10 June 2004
Prof TASSAING, Thierry	CNRS, Universite Bordeaux I, France, 3 September 2004
Prof ROSSKY, Peter J.	Vis Prof of JSPS, University of Texas at Austin, USA, 4, 9 - 10 September 2004
Prof NELLIS, William J.	President of AIRAPT (International Association for the Advancement of High Pressure Science and Technology), Harvard University, USA, 13 September 2004

Scope of Research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR under extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Static and dynamic NMR of endocrine disruptors, anesthetics, peptides, and proteins in lipid bilayer membranes are also investigated.

Research Activities (Year 2004)

Presentations

A Challenge to Chemical Evolution Using Hot Water, Nakahara M, Workshop on Chemistry of Biological Processes Created by Water and Biomolecules, 9 January.

Structure, Dynamics, and Reactions in Supercritical Water Studied by NMR and Computer Simulation, Nakahara M, The 14th International Conference on the Properties of Water and Steam, Kyoto, 30 August.

Development of a High-Temperature NMR Probe: Toward Temperature Homogeneity, Multinuclear Measurement, and High Magnetic Field Gradient, Nakahara M, Matubayasi N, Wakai C, and Yoshida K, The 14th International Conference on the Properties of Water and Steam, Kyoto, 2 September.

Hydrothermal C1 Chemistry: Equilibrium Study, Matubayasi N, Wakai C, Yoshida K, et al., The 14th International Conference on the Properties of Water and Steam, Kyoto, 2 September, and **39** related presentations.

Location and Side-Chain Conformation of a Neuropeptide, Achatin-I in Phospholipid Bilayer Membrane: A High-Resolution NMR Study, Kimura T, Okamura E, Matubayasi N, and Nakahara M, The Biophysical Society 48th Annual Meeting, USA, 18 February, and **2** related presentations.

Grants

Nakahara M, Development of Multinuclear, High-Temperature, and Diffusion-Measurable NMR Probe and Molecular Analysis of Dynamics of Supercritical Aqueous Solutions, Grant-in-Aid for Scientific Research (A) (2), 1

NMR Spectroscopic Evidence for an Intermediate of Formic Acid in the Water-Gas-Shift Reaction

The water-gas-shift (WGS) reaction ($CO + H_2O \rightleftarrows CO_2 + H_2$) is investigated in connection to formic acid. Using NMR spectroscopy, the reversible decomposition pathways of formic acid to both sides of the WGS reaction are studied in hot water at 240-260°C. This reversibility strongly suggests that formic acid exists as an intermediate in the WGS reaction, and it is indeed demonstrated that carbon monoxide is treated in hot water to produce formic acid. The present result enables us to generate and store hydrogen in the liquid form of formic acid and to transform formic acid to hydrogen in water by tuning the thermodynamic conditions.

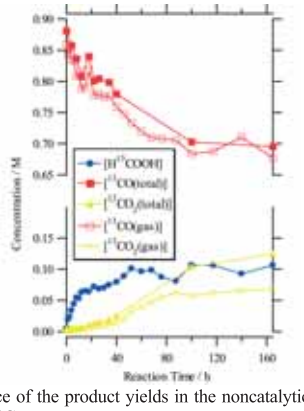

Figure 1. The time dependence of the product yields in the noncatalytic water-gas-shift reaction at 250°C.

Yoshida K, Wakai C, Matubayasi N, Nakahara M, *J. Phys. Chem. A,* **108**, 7479-7482 (2004).

Lipid Membrane Dynamics and Drug Transport by High-Field-Gradient, High-Resolution NMR

Diffusion rates of lipids and a trapped endocrine disruptor, bisphenol A (BPA), are determined in fluid lipid membranes. We have specially designed a high-power field gradient probe for a 600 MHz NMR apparatus. The probe can exert a field gradient up to 1350 G/cm, which is sufficient to monitor dynamic events in highly viscous cell membrane. The motion of BPA is not rapid in membrane. The mobility is almost equal to the membrane lipid diffusion. It is in sharp contrast to the motion of benzene and toluene in membrane, which diffuse faster than the lipid matrices (Figure 2). The slowdown of BPA and lipid motions is leveled off in 100- and 400-nm vesicles, although the hydrodynamic continuum model gives the molecular motion slowed inversely to the lipid particle size. Instead, the limited motion is related to the *intra*-membrane fluidity. Diffusion rates of alkylbenzenes and alkylphenols, anesthetics, and channel peptides are also successfully determined in membranes.

Okamura E, Wakai C, Matubayasi N, Sugiura Y, Nakahara M, *Phys. Rev. Lett.,* **93**, 248101 (2004).

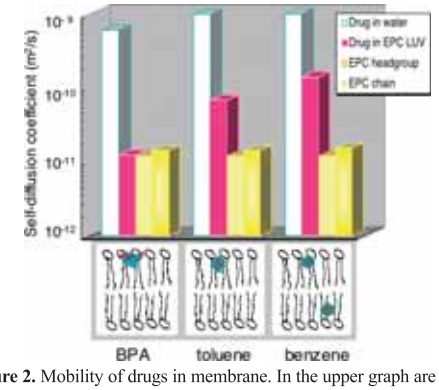

Figure 2. Mobility of drugs in membrane. In the upper graph are the self-diffusion rates of drugs in water (white) and in 100-nm vesicles (red) at 30°C, together with the mobility of membrane lipid head group (light yellow) and the chain core (yellow). Location of the drug in membrane is shown schematically in the bottom by the space filling model with H, blue; C, grey; and O, red.

April 2003 - 31 March 2006.

Nakahara M, "Free-Energy Analysis of Nanoscale Aggregates of Molecules in the Method of Energy Representation", National Research Grid Initiative Project, 1 April 2003 - 31 March 2008.

Nakahara M, Ion Transport Mechanism in Phospholipid Bilayer Membranes by Thermal Fluctuation, Grant-in-Aid for Exploratory Research, 1 April 2004 - 31 March 2005.

Matubayasi N, Collaboratory on Electron Correlations - Toward a New Research Network between Physics and Chemistry, Grant-in-Aid for Creative Scientific Research, 1 April 2001 - 31 March 2006.

Matubayasi N, Molecular Studies of Solvation Effect on the Structure and Fluctuation of Biomolecules and their Aggregates, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2003 - 31 March 2008.

Okamura E, Transport of Endocrine Disruptors in Phospholipid Bilayer Membranes, Grant-in-Aid for Scientific Research (C) (2), 1 April 2002 - 31 March 2004.

Wakai C, Inversion of Magnitude Relation of Translational and Rotational Diffusion Coefficients for Organic Acids and Their Ions in Aqueous Solutions, Grant-in-Aid for Scientific Research for Young Scientists (B), 1 April 2002 - 31 March 2004.

Award

Nakahara M, Prize of The Japan Society of High Pressure Science and Technology, 2004, NMR Studies on Water and Aqueous Solution under High Pressure and Supercritical Conditions, 10 October.